

## NO DRAWINGS

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## (54) TREATMENT OF GAS MIXTURES

(71) We, CELANESE CORPORATION, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of gas mixtures and, more particularly, to the separation of carbon dioxide from gas mixtures containing it.

An aqueous solution of potassium carbonate can be used for absorbing carbon dioxide from gas mixtures containing it. If the absorption is effected at normal temperatures and pressures the absorbed carbon dioxide can be recovered and the spent potassium carbonate solution rendered fit for a further absorption stage by boiling the spent solution. To make such a process commercially useful expensive heat exchange equipment would be necessary and, accordingly, what is known as the "hot carbonate process" is favoured. In the latter process the carbon dioxide is absorbed in hot potassium carbonate solution under superatmospheric pressure and regeneration of the spent solution effected by reducing the pressure on the solution assisted by steam stripping. Although this process is widely used it has disadvantages and, in particular, severe corrosion is encountered and the amount of steam used in stripping carbon dioxide from the spent absorption solution is excessive.

The present invention comprises a process for the separation of carbon dioxide from a gas mixture containing it, by scrubbing the gas mixture with an aqueous solution which absorbs carbon dioxide and subsequently subjecting the spent solution to a regenerating operation at a temperature and/or pressure sufficiently different from that used in the scrubbing operation to cause release of carbon dioxide, wherein the aqueous solution has the

composition of one obtained by dissolving in water orthoboric acid and potassium hydroxide in the proportions of from 0.6 to 4.0 moles of orthoboric acid per mole of potassium hydroxide.

The scrubbing solution of the present invention has been found to be superior to a potassium carbonate solution in several respects. Thus, the solution gives rise to less corrosion at least partly because the pH of the solution, whether spent or fresh or regenerated, is generally lower than that of a similar potassium carbonate solution and partly, it is believed, by reason of the boron compounds present. Furthermore, less heat is required in order to regenerate the scrubbing solution of the invention than is needed with a potassium carbonate solution, especially when high ratios (2:1 and higher) of boric acid to potassium hydroxide are used in forming the solution. Not only is less heat required for regeneration but it can be performed at lower temperatures, so that operation of a substantially isothermal process is possible at a lower overall temperature, i.e. for both absorption and regeneration.

Another advantage of the scrubbing solution of the invention is that it is more selective in removing carbon dioxide from a gas mixture where hydrocarbons are present than is potassium carbonate. For example, when removing carbon dioxide from admixture with ethylene a certain amount of ethylene is absorbed in the scrubbing solution but less than is the case when using a potassium carbonate solution of similar strength. The economic superiority of the scrubbing solution of the invention is shown by the fact that the solution will absorb, per unit of potassium plus boron, more carbon dioxide per volume of solution than will a potassium carbonate solution per unit of potassium; in other words, an aqueous solution of potassium carbonate having 10 weight per cent potassium therein will absorb less carbon dioxide at a given temperature and pressure than will a scrubbing solution containing 10 weight per cent of potas-

5 sium and boron combined, for example 4 weight per cent boron and 6 weight per cent potassium. One further advantage of the present invention is that, when a purge of the scrubbing solution is required due to the build-up of impurities, the boron and potassium compounds can be more easily recovered by simple crystallisation by cooling than can be potassium carbonate. The reason for this is that, at least in the spent solution withdrawn from the absorber, the solubilities at room temperature of the boron and potassium compounds in the scrubbing solutions are considerably lower than those of the compounds present when using a potassium carbonate solution. This is true even though the solubilities of the compounds present in the solutions of the invention and those present when potassium carbonate is used are comparable at temperatures above 60°C. Due to the fact that the solubility of the boron and potassium compounds present in the spent solutions of the invention decreases rapidly as the temperature drops below 60°C, a large amount of them can be recovered easily by cooling to room temperature the spent solution withdrawn from the absorption step.

10 The exact nature of the reactions involved in the absorption and regeneration steps in the process of the invention is not understood. Analyses have failed to reveal the presence of any carbonate ion in the regenerated scrubbing solutions and have also failed to reveal the presence of any bicarbonate ions in spent scrubbing solutions except at low ratios of orthoboric acid to potassium hydroxide. It is possible that the absence of bicarbonate ion at the higher ratios of orthoboric acid to potassium hydroxide accounts for the fact that less heat is required for regeneration of the spent solution.

15 It has been found best to use a scrubbing solution made by dissolving in water at least 2 moles of orthoboric acid per mole of potassium hydroxide and, especially, from 2.3 to 3.4 moles of orthoboric acid per mole of potassium hydroxide. The higher the concentration of the solution the more carbon dioxide it will absorb but, in practice, the solubility of the substances present is the limiting factor and it is, in general, best to use solutions containing less than 10 weight per cent, preferably from 2.0 to 7.0 weight per cent, of boron calculated as the element.

20 The carbon dioxide separation operation can be carried out using any of the techniques suitable for use with a potassium carbonate solution as scrubbing liquid. Although a batch operation can be used it is best to employ a continuous process carried out in the manner commonly used in the hot carbonate process, the absorption step and the regeneration step taking place in separate zones or vessels with the scrubbing solution being continuously withdrawn from the absorption zone and con-

tinuously recycled between the absorption zone and regeneration zone. To maintain a high enough concentration of active constituents in the scrubbing solution to make a good rate of carbon dioxide possible, the temperature in the absorption zone, regardless of the manner of carrying out the invention, should be above 65°C, for example from 70°C to 160°C, the preferred range being from 90°C to 120°C. The pressure during the absorption must be sufficient to prevent boiling of the solution and may range, for example, from atmospheric to 30 atmospheres absolute. Preferably, however, the pressure in the absorption zone is above four atmospheres, e.g. from 6 to 25 atmospheres absolute.

25 The temperature and/or the pressure for the regeneration will be varied from that used during the absorption in order to cause evolution of the carbon dioxide from the spent solution. As already stated, however, the technique utilised in the hot carbonate process is preferred so that the temperatures of the regeneration zone and the absorption zone are not widely different, i.e. within 30°C of each other, so that no substantial amount of heating or cooling of the scrubbing solution is needed between the absorption zone and the regeneration zone. Thus the preferred temperatures of the regeneration zone may also be within the range of 70°C to 160°C and, especially, 90°C to 120°C, the regeneration zone being operated at a substantially lower pressure than the absorption zone. Pressures of from 0.9 to 4.0 atmospheres absolute are, in general, suitable in the regeneration zone with pressures within the ranges of atmospheric to two atmospheres absolute being preferred. The regeneration of the spent scrubbing solution can be, and is preferably, accompanied by boiling and steam stripping at pressures corresponding to solution boiling temperatures with the steam being generated in the bottom section of the stripper or regenerator column by means of an external source of heat, such as a steam coil, and/or by injection of live steam; carbon dioxide and steam pass overhead and can be cooled to condense the steam and the condensate, where it is generated within the column, being added to the regenerated scrubbing solution. The evolution of the carbon dioxide from solution is an endothermic reaction and therefore the temperature of the solution being regenerated will drop unless some heat is supplied to the column.

30 In operating the absorption zone of a continuous process, the proper ratio of gas mixture to scrubbing solution can be maintained by analysis of the vent gas from the absorption zone, an undesirably high level of carbon dioxide needing correction by decreasing the feed rate of the gas mixture or by increasing the feed rate of the scrubbing solution.

35 The process of the invention can be used to separate carbon dioxide from gas mixtures in

which it is present in any appreciable concentration, although the process is most usefully employed for treating gas mixtures containing at least 10 mole per cent carbon dioxide, for example 10 to 90 mole per cent carbon dioxide. The other gases present may be, for example, ethylene, oxygen, propylene, methane, carbon monoxide, nitrogen or hydrogen. For example, the gas mixture being treated may be a synthesis gas (hydrogen-carbon monoxide mixtures) produced by coal gasification or natural gas reforming, or a hydrogen-carbon dioxide mixture produced by the water gas shift reaction. In view of the high temperatures and pressures at which the absorption step of the invention may be carried out, the invention can, with advantage, be employed for the purification of synthesis gas, for the Fischer-Tropsch synthesis, the methanol synthesis and the so-called "Oxo" synthesis which are made or used at high temperatures and pressures. Other gas mixtures from which carbon dioxide can be removed by the process of the invention are naturally occurring gaseous hydrocarbons which are contaminated with carbon dioxide and gas mixtures from the partial oxidation of hydrocarbons. The invention is especially useful for use in separating carbon dioxide from a gas mixture containing from 10 to 50 mole per cent carbon dioxide and 50 to 90 mole per cent of hydrocarbons. In addition to containing such amounts of carbon dioxide and hydrocarbons there may be other constituents, e.g. oxygen and nitrogen. These other constituents may be either reactive with the scrubbing solution or inert and, if reactive, it is preferred that they be present in amounts of less than 5 mole per cent; in these circumstances it is best to remove a purge stream from the scrubbing solution at some point in the cycle, to prevent a build-up of impurities, and replace it with fresh solution.

The following Examples illustrate the invention:—

#### Example 1.

The plant employed comprised an absorption tower 10 metres high and 30 centimetres in diameter and a stripping tower 8 metres high and 35 centimetres in diameter, both towers being packed with 4-centimetre ceramic interlock saddles. A feed gas resulting from the production of vinyl acetate from ethylene and acetic acid and containing 20 mole per cent of  $\text{CO}_2$ , 5 mole per cent of oxygen, 5 mole per cent of nitrogen, 70 mole per cent of ethylene and traces of acetic acid and vinyl acetate was fed as a side stream to the lower part of the absorption tower at a rate of 2080 litres per minute, as measured at 25°C and atmospheric pressure. An aqueous scrubbing solution was fed as a side stream to an upper point in the tower at a rate of 38 litres per minute, the scrubbing solution being one formed by dissolving in water sufficient potas-

sium hydroxide and orthoboric acid, in the ratio of three moles of orthoboric acid per mole of potassium hydroxide, for the solution to contain 6.3 weight per cent boron and 7.43 weight per cent potassium, calculated as the elements.

The absorption tower was operated at 105°C and 9.5 atmospheres absolute to give an overhead gas stream comprising 86 mole per cent of ethylene, 2 mole per cent of carbon dioxide, 6 mole per cent of oxygen and 6 mole per cent of nitrogen. Spent scrubbing solution was continuously withdrawn from the bottom of the absorption tower and passed without cooling to the top of the stripping tower which was operated at 105°C and 1.25 atmospheres pressure absolute. Steam for stripping was generated by a steam coil in the reboiler section of the stripping tower. The stream removed overhead from the stripping tower was passed to a condenser where steam was condensed and returned to the stripper as reflux. The vent gas from the condenser contained 97 mole per cent of carbon dioxide and 1.5 mole per cent of ethylene.

From the bottom of the stripping tower a stream of regenerated scrubbing solution was withdrawn and split into two portions, the major portion being returned to the top of the absorption tower without cooling while the minor portion was recycled to just above the midpoint of the stripping tower. To this minor portion being returned to the stripping tower fresh scrubbing solution was periodically added to account for that purged periodically, the purge stream being taken from the stream of spent solution removed from the bottom of the absorption tower when the level of potassium acetate in the system became too high.

#### Example 2.

In order to demonstrate the effect of varying some of the conditions in the process of the invention, four sets of trials were carried out using a two-litre stainless steel bomb fitted with pressure and temperature gauges and connected *via* a valve to a cylinder of pure carbon dioxide under high pressure. In each trial one litre of scrubbing solution was placed in the bomb and then the bomb pressurised with carbon dioxide to 7.8 atmospheres absolute and shaken for several minutes so as to allow absorption of carbon dioxide, as indicated by a drop in bomb pressure. This was repeated several times until after pressurising to 7.8 atmospheres absolute no decrease in pressure was noted upon shaking of the bomb. The pressure on the bomb was then reduced to atmospheric pressure, the volume of carbon dioxide evolved being measured at 25°C and atmospheric pressure. Each trial was repeated several times and the average amount of carbon dioxide absorbed and desorbed for a given scrubbing solution taken for each set of trials. The temperature of

the bomb was maintained constant at 100°C during both the absorption and the desorption of each trial. The results obtained are presented in the following Table, the volume of carbon dioxide absorbed and desorbed being corrected to account for the dead volume of the bomb which was determined by a trial with one litre of distilled water.

After the last absorption cycle in the last trial of each set the bomb was first cooled under 7.8 atmospheres pressure to 25°C and then the pressure was reduced to atmospheric with little or no carbon dioxide being evolved. A sample of the scrubbing solution having the CO<sub>2</sub> therein was then removed, the sample

shaken to release excess CO<sub>2</sub> and the pH of the solution noted. This sample was then heated slowly at atmospheric pressure to determine the temperature to which it was necessary to heat the sample in order to cause evolution of the carbon dioxide to regenerate the solution. The temperature range in which evolution of carbon dioxide began and ended during the heating is given in the Table.

For the purposes of comparison a set of trials were also carried out using a 25 weight per cent potassium carbonate solution as the scrubbing solution, the results obtained appearing in the Table under the heading "Comparison Set".

	Set 1	Set 2	Set 3	Set 4	Comparison Set
Scrubbing Solution:—					
(a) Wt % Boron	3.2%	3.2%	6.4%	3.2%	—
(b) Wt. % Potassium	3.7%	5.5%	7.4%	11.1%	13.8%
Total (a) + (b)	6.9%	8.7%	13.8%	14.3%	13.8%
mole ratio H <sub>2</sub> BO <sub>3</sub> /KOH	3/1	2/1	3/1	1/1	—
Volume CO <sub>2</sub> absorbed and desorbed, litres	5.7	5.6	13.6	11.6	9.3
pH of scrubbing solution saturated with CO <sub>2</sub> at 25°C.	7.8	7.3	7.5	7.8	9.0
CO <sub>2</sub> evolution temperatures at atm. press., °C.	60—80	60—80	60—80	70—98	90—98

### Example 3.

In order to demonstrate that the process of the invention can be operated isothermally at lower temperatures more efficiently than can a potassium carbonate process, trials under the conditions of Set 4 and the Comparison Set of Example 2 were repeated at temperatures of 65°C. Under the conditions of Set 4 approximately 5.0 litres of carbon dioxide, measured at 25°C and atmospheric pressure, were absorbed and desorbed whereas in the potassium carbonate trials an average of only one litre of carbon dioxide was absorbed and described.

### WHAT WE CLAIM IS:—

1. Process for the separation of carbon dioxide from a gas mixture containing it, by scrubbing the gas mixture with an aqueous solution which absorbs carbon dioxide and subsequently subjecting the spent solution to a regenerating operation at a temperature and/or pressure sufficiently different from that used in the scrubbing operation to cause release of carbon dioxide, wherein the aqueous solution has the composition of one obtained by dissolving in water orthoboric acid and potassium

hydroxide in the proportions of from 0.6 to 4.0 moles of orthoboric acid per mole of potassium hydroxide.

2. Process according to Claim 1, wherein the aqueous solution used is one made by dissolving in water orthoboric acid and potassium hydroxide in the proportions of from 2.3 to 3.4 moles of orthoboric acid per mole of potassium hydroxide and contains from 2 to 7 weight per cent of boron calculated as the element.

3. Process according to Claim 1 or 2, wherein absorption and regeneration are carried out at temperatures of from 70°C to 160°C and within 30°C of each other and the pressure during absorption is maintained at from 6 to 25 atmospheres absolute and during regeneration at from 0.9 to 4.0 atmospheres absolute.

4. Process according to Claim 1, 2 or 3, wherein the process is carried out continuously with absorption and regeneration being accomplished in separate zones with the aqueous solution being continuously withdrawn from the absorption zone and continuously recycled between the absorption zone and the regeneration zone.

5. Process according to Claim 1, 2, 3 or 4, wherein spent aqueous solution is subjected to steam stripping in regeneration under a pressure corresponding to solution boiling temperatures ranging from 70°C to 160°C.

6. Process according to any of the preceding claims, wherein said gas mixture contains from 10 to 50 mole per cent of carbon dioxide and from 50 to 90 mole per cent of hydrocarbons.

7. Process according to Claim 6, wherein said gas mixture is one resulting from a pro-

cess for the production of vinyl acetate from ethylene and acetic acid and contains from 50 to 90 mole per cent ethylene.

8. Process for the separation of carbon dioxide from a gas mixture containing it, substantially as hereinbefore described.

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